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Gaya Kanishka Marasinghe

Peter C. Ezekwenna

William Joseph James

*Missouri University of Science and Technology, wjames@mst.edu*

Gary J. Long

*Missouri University of Science and Technology, glong@mst.edu*

*et. al. For a complete list of authors, see [https://scholarsmine.mst.edu/chem\\_facwork/777](https://scholarsmine.mst.edu/chem_facwork/777)*

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# Neutron diffraction and Mössbauer spectral study of the $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$ solid solutions

G. K. Marasinghe, Peter C. Ezekwenna, W. J. James, Gary J. Long, and O. A. Pringle  
*Departments of Physics and Chemistry and the Graduate Center for Materials Research, University of Missouri-Rolla, Rolla, Missouri 65401-0249*

Z. Hu and W. B. Yelon  
*University of Missouri Research Reactor, University of Missouri-Columbia, Columbia, Missouri 65211*

F. Grandjean  
*Institut de Physique, Université de Liège, B-4000 Sart-Tilman, Belgium*

Three samples of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$ , with  $x$  equal to 0.0, 0.3, and 2.8, with the  $\text{Th}_2\text{Zn}_{17}$ -type rhombohedral structure, have been studied by powder x-ray and neutron diffraction, magnetic measurements, and Mössbauer spectroscopy.  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  were synthesized by induction melting stoichiometric amounts of the constituent elements, whereas  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  was synthesized by methane-derived gas phase insertion of carbon into finely ground  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  at 600 K. The neutron diffraction determined titanium site occupancies are similar in both  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  in which titanium preferentially occupies the  $6c$  transition metal site. In contrast, the titanium occupancies in  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  are markedly different in that titanium avoids the  $6c$  transition metal site and randomly occupies the other three transition metal sites. This difference in occupancies most likely occurs because the titanium diffusion rate during the quenching of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  is affected by the presence of carbon in the melt. Even though the unit cell volume of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  is larger than that of  $\text{Nd}_2\text{Fe}_{17}\text{N}_3$ , the 615 K Curie temperature of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  is much lower than the 746 K Curie temperature of  $\text{Nd}_2\text{Fe}_{17}\text{N}_3$ . This is an indication that the volume expansion, which occurs upon nitrogenation of  $\text{R}_2\text{Fe}_{17}$ , is not the only factor which contributes to the increase in the Curie temperature. The Mössbauer spectra of  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  confirm the high preferential titanium occupancy of the  $6c$  site. At 85 K the weighted average hyperfine field of  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  is approximately 263 kOe, a value which is 33 kOe smaller than that in  $\text{Nd}_2\text{Fe}_{17}$ . The 85 K Mössbauer spectrum of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  is virtually identical to that of  $\text{Nd}_2\text{Fe}_{17}$  and indicates an approximately random titanium occupancy of the four transition metal sites. © 1996 American Institute of Physics. [S0021-8979(96)36608-4]

## I. INTRODUCTION

The discovery<sup>1</sup> that the addition of interstitial nitrogen dramatically increases the Curie temperature of  $\text{R}_2\text{Fe}_{17}$  and changes the magnetocrystalline anisotropy from basal in  $\text{Sm}_2\text{Fe}_{17}$  to axial in  $\text{Sm}_2\text{Fe}_{17}\text{N}_3$  has led to a renewed interest in the  $\text{R}_2\text{Fe}_{17}$  compounds. Even though the Curie temperatures<sup>1</sup> of the resulting  $\text{R}_2\text{Fe}_{17}\text{N}_x$  compounds are significantly higher than those of the  $\text{R}_2\text{Fe}_{14}\text{B}$  compounds, they are lower than those of the previous generation of permanent magnets based on  $\text{SmCo}_5$ . However, the interstitially modified  $\text{Sm}_2\text{Fe}_{17}\text{C}_x$  and  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  compounds have high energy products,<sup>2</sup> approximately 80 kJ/m<sup>3</sup>, at room temperature and Curie temperatures high enough to make them useful in a wide variety of magnetic applications. Unfortunately, interstitial  $\text{R}_2\text{Fe}_{17}\text{N}_x$  and  $\text{R}_2\text{Fe}_{17}\text{C}_x$ , prepared by gas–solid reactions, are thermally unstable, decomposing at temperatures slightly above their Curie temperatures.<sup>3</sup> In contrast, recent studies<sup>4,5</sup> have shown that certain  $\text{R}_2(\text{Fe},\text{M})_{17}\text{C}_x$  solid solutions, where M is Ga, Al, or Si, which were synthesized by a solid–solid reaction, exhibit high thermal stability. In this article we report the results of a crystallographic and magnetic study of three  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$  samples, with  $x$  equal to 0.0, 0.3, and 2.8.

## II. EXPERIMENTAL METHODS

$\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  were prepared from 99.9% pure elements by induction melting followed by annealing at 950 °C for 120 h.  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  was synthesized by methane-derived gas phase insertion of carbon into finely ground  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  at 600 K. The phase purity of the samples was checked by x-ray diffraction with  $\text{Cu } K_\alpha$  radiation on a Philips PW 1800/10 x-ray diffractometer equipped with a single crystal graphite monochromator. The Curie temperatures of the samples were measured by a SQUID magnetometer. The powder neutron diffraction patterns were measured in thin walled vanadium containers in approximately 24 h each at 295 K with 1.4766 Å neutrons, and were refined by the Rietveld method on the basis of the  $\text{Nd}_2\text{Fe}_{17}$  structure.<sup>6</sup> The titanium and carbon site occupancies refined to an accuracy of approximately  $\pm 2\%$ .

The Mössbauer spectra were measured at 85 and 295 K on a constant acceleration spectrometer which utilized a room temperature rhodium matrix cobalt-57 source and was calibrated at room temperature with  $\alpha$ -iron foil. The typical linewidth of the outer lines of  $\alpha$ -iron was 0.26 mm/s. Mössbauer absorbers, with a typical thickness of 30 mg/cm<sup>2</sup>, were prepared from powders which had been sieved to a 0.038 mm or smaller particle diameter. The spectra were fitted with

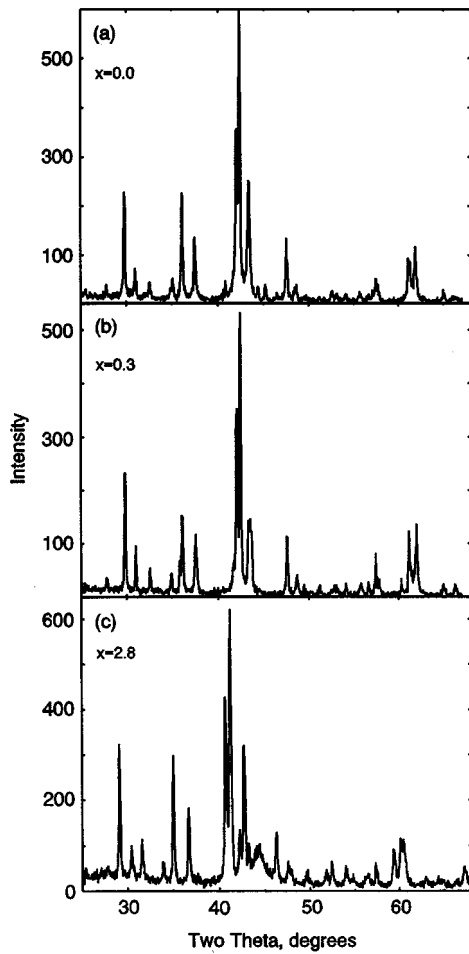


FIG. 1. X-ray diffraction patterns of (a)  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ , (b)  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ , and (c)  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ .

seven magnetic sextets corresponding to the seven magnetically inequivalent iron sites expected<sup>7</sup> for a basal orientation of the magnetization. Details of this fitting procedure have been published elsewhere.<sup>8,9</sup> The magnetic structures of these  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$  samples have been determined by neutron diffraction studies<sup>10</sup> to be basal, consistent with the magnetic structures of other  $\text{Nd}_2\text{Fe}_{17}$  based interstitial compounds.<sup>8</sup>

### III. RESULTS AND DISCUSSION

The Curie temperatures are 380, 440, and 615 K for  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$  with  $x$  equal to 0.0, 0.3, and 2.8, respectively.

X-ray diffraction patterns, see Fig. 1, indicate that the three samples crystallize in the rhombohedral  $\text{Th}_2\text{Zn}_{17}$ -type structure. However, a small amount of  $\alpha$ -iron is observed in  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ . The lattice parameters, atomic positional parameters, and site occupancies, obtained from the neutron diffraction data, are given in Table I. As can be seen in this table, the replacement of one iron by titanium in  $\text{Nd}_2\text{Fe}_{17}$  increases slightly the unit cell volume. A similar small increase has been observed in the  $\text{R}_2\text{Fe}_{14-x}\text{Ti}_x\text{B}$  solid solutions.<sup>11</sup> However, in contrast, the  $857 \text{ \AA}^3$  unit cell volume of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  is much larger than the  $802 \text{ \AA}^3$  volume of  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and even larger than the  $844 \text{ \AA}^3$  volume<sup>12</sup> of  $\text{Nd}_2\text{Fe}_{16}\text{N}_{2.7}$ , whereas the 615 K Curie temperature of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  is much lower than the 746 K value<sup>13</sup> of  $\text{Nd}_2\text{Fe}_{17}\text{N}_3$ . This indicates that the volume expansion which occurs upon nitrogeneration or carbonation of  $\text{R}_2\text{Fe}_{17}$  is not the only factor responsible for the accompanying increase in the Curie temperature.

As seen in Table I, the titanium site occupancies in  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  are similar and titanium preferentially occupies the  $6c$  transition metal site. In contrast, the titanium site occupancies in  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  are markedly different in that titanium appears to avoid the  $6c$  site and almost randomly occupies the other three transition metal sites. The

TABLE I. Room temperature powder neutron diffraction results for  $\text{Nd}_2\text{Fe}_{17}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_x$ .

| Parameter             |                       | $\text{Nd}_2\text{Fe}_{17}$ <sup>a</sup> | $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ | $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ | $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ |
|-----------------------|-----------------------|--|--------------------------------------|---|---|
| Lattice parameters    | $a$ (Å)               | 8.6002(1)                                | 8.6042(3)                            | 8.6452(5)                                   | 8.8385(6)                                   |
|                       | $c$ (Å)               | 12.4835(2)                               | 12.5133(5)                           | 12.4875(9)                                  | 12.6662(11)                                 |
|                       | $V$ (Å <sup>3</sup> ) | 799.62(3)                                | 802.28(9)                            | 808.27(15)                                  | 856.9(2)                                    |
| Positional parameters | Nd, $6c$ , $z$        | 0.3426(3)                                | 0.3429(6)                            | 0.3451(7)                                   | 0.3417(6)                                   |
|                       | Fe/Ti, $6c$ , $z$     | 0.0957(2)                                | 0.0973(7)                            | 0.0956(5)                                   | 0.0967(12)                                  |
|                       | Fe/Ti, $18f$ , $x$    | 0.2882(1)                                | 0.2934(3)                            | 0.2886(4)                                   | 0.2847(4)                                   |
|                       | Fe/Ti, $18h$ , $x$    | 0.1682(1)                                | 0.1680(2)                            | 0.1691(3)                                   | 0.1736(3)                                   |
|                       | Fe/Ti, $18h$ , $z$    | 0.4893(1)                                | 0.4907(2)                            | 0.4891(4)                                   | 0.4865(4)                                   |
|                       | C, $18g$ , $x$        | ...                                      | ...                                  | 0.880 <sup>b</sup>                          | ...   |
| Percent occupancy     | Ti, $6c$              | ...                                      | 38                                   | 1   | 37  |
|                       | Ti, $9d$              | ...                                      | 0                                    | 5   | 3   |
|                       | Ti, $18f$             | ...                                      | 3                                    | 6   | 0   |
|                       | Ti, $18h$             | ...                                      | 2                                    | 8   | 6   |
|                       | C, $9e$               | ...                                      | ...                                  | 6   | 99  |
|                       | C, $18g$              | ...                                      | ...                                  | 2   | 0   |
| Fit parameters        | $R_p$ (%)             | ...                                      | 6.6                                  | 5.3   | 4.6   |
|                       | $\chi^2$              | ...                                      | 4.3                                  | 5.2   | 2.7   |

<sup>a</sup>Data taken from Ref. 9.

<sup>b</sup>Parameter determined by manual iteration refinement.

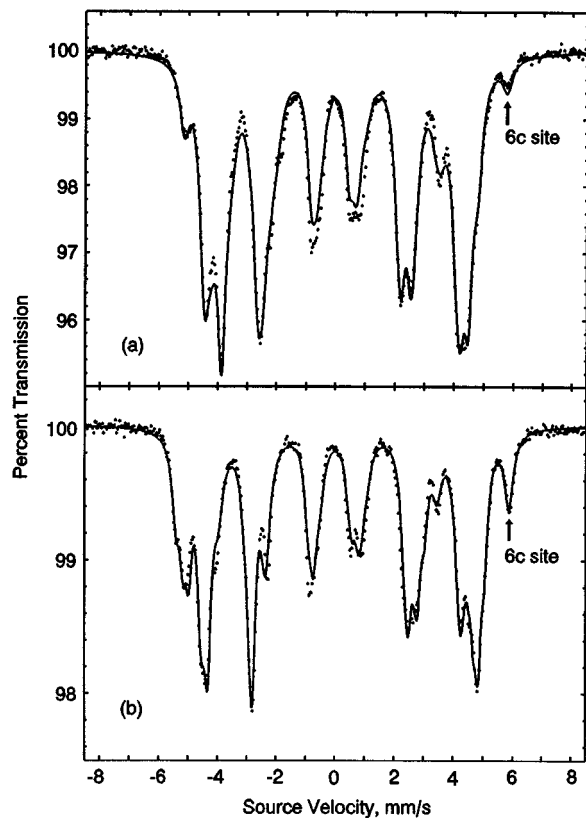


FIG. 2. The Mössbauer spectra of (a)  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ , and (b)  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  obtained at 85 K.

difference in titanium occupancies in the two carbided samples can be attributed to the difference in their preparation. The similar titanium occupancies in  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  are expected because  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  was synthesized by methane-derived gas phase insertion of carbon at 600 K into fine powders of the induction melted  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$ . Iron and titanium have 12 coordinate metallic radii of 1.26 and 1.47 Å, respectively, and, as a consequence of its larger radius, titanium preferentially occupies the 6c iron site in  $\text{Nd}_2\text{Fe}_{17}$ , the iron site with the largest Wigner–Seitz cell volume.<sup>8</sup> None of the metal atoms are appreciably mobile at 600 K and thus the metal occupancies in  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$  are expected and found to be similar. In contrast to the preparation of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ , carbon was present in the melt during the induction melting preparation of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ . Carbon has a very high affinity for titanium and this affinity influences the mobility of the carbon and titanium atoms in the melt.<sup>14</sup> Because of this affinity one expects, as is observed, to find that the titanium prefers the

18f and 18h sites, the sites which have carbon near-neighbors. Consequently, one would expect the titanium occupancies after quenching of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  to be different from those in  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ .

The 85 K Mössbauer spectra of  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  and  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ , see Fig. 2, confirm the difference in titanium occupancies of the 6c transition metal site. In these Mössbauer spectra the highest velocity absorption line is the sixth line of the 6c sextet. As may be seen in Fig. 2, the absorption area of the 6c sextet of the  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  spectrum is smaller than in  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$  and confirms that the titanium 6c occupancy in  $\text{Nd}_2\text{Fe}_{16}\text{Ti}$  is higher than in  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ . The weighted averaged hyperfine fields at 85 K are 263, 292, and 254 kOe for the samples with  $x$  equal to 0.0, 0.3, and 2.8, respectively. At 295 K, the weighted average hyperfine fields are 189, 191, and 227 kOe, respectively. The dependence of the weighted averaged hyperfine field at 295 K on the carbon content follows that of the Curie temperature. However,  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{0.3}$ , whose Curie temperature is much lower than that of  $\text{Nd}_2\text{Fe}_{16}\text{TiC}_{2.8}$ , has the highest hyperfine field at 85 K.

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